

Adhesive Bond Failures in Aircraft Honeycomb-Sandwich Composites

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13. ABSTRACT

Military aircraft have experienced numerous failures of the adhesive bond in aluminum honeycomb-sandwich composites. Though these failures have not been catastrophic, they have been very costly to repair. Because adhesive bonding has advantages over other means of fastening, an improvement in the durability and reliability of the bond is desired in order that continued and increased use may be made of this type of construction.

To a large extent, these failures appear to be attributable to the sensitivity of the bonded joint to moisture, as manifested by displacement and/or corrosion at the bonded interface. Bond failure also appears to be partially due to the brittleness, void content, and inhomogeneities in the adhesive.

Examination of a typical aircraft adhesive revealed numerous voids in the cured bond. These voids appear to originate from air entrapped in the adhesive during its manufacture and/or from volatiles evolved during the cure. These voids were also shown to be interconnected by the filaments of the cloth used as the carrier of the adhesive resin.

Since most of the honeycomb-sandwich delaminations and adhesive failures have been accompanied by corrosion of the bonded aluminum skin, the effectiveness of various treatments and anticorrosive adhesive primers in protecting aluminum has been examined by electrochemical techniques and salt fog exposures. The electrochemical studies, in which potential distribution curves are obtained for treated panels, provide quantitative data on the

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<p>effectiveness and the nature of the protection. These studies have tentatively indicated that (a) certain pigments incorporated into an epoxy matrix provide corrosion protection, while others enhance corrosion, (b) anticorrosive chemical treatments of the metal surface may lose effectiveness under some conditions, (c) the standard $\text{Na}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ treatment that is given most aluminum alloys before bonding may actually increase corrosion susceptibility, and (d) cladding (Alclad) is a desirable surface to bond to.</p> <p>Efforts have been made to synthesize adhesive resins with reduced brittleness and greater moisture resistance. Two new linear epoxy resins were prepared which had lower moisture adsorption than a typical aircraft adhesive. Although these new resins contained chlorine and bromine, their thermal stability was not adversely affected over the temperature range of interest, i.e., up to a maximum of 235°C.</p>						

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ABSTRACT

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Since most of the honeycomb-sandwich delaminations and adhesive failures have been accompanied by corrosion of the bonded aluminum skin, the effectiveness of various treatments and anticorrosive adhesive primers in protecting aluminum has been examined by electrochemical techniques and salt fog exposures. The electrochemical studies, in which potential distribution curves are obtained for treated panels, provide quantitative data on the effectiveness and the nature of the protection. These studies have tentatively indicated that (a) certain pigments incorporated into an epoxy matrix provide corrosion protection, while others enhance corrosion, (b) anticorrosive chemical treatments of the metal surface may lose effectiveness under some conditions, (c) the standard $\text{Na}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ treatment that is given most aluminum alloys before bonding may actually increase corrosion susceptibility, and (d) cladding (Alclad) is a desirable surface to bond to.

Efforts have been made to synthesize adhesive resins with reduced brittleness and greater moisture resistance. Two new linear epoxy resins were prepared which had lower moisture adsorption than a typical aircraft adhesive. Although these new resins contained chlorine and bromine, their thermal stability was not adversely affected over the temperature range of interest, i.e., up to a maximum of 235°C.

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AUTHORIZATION

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ADHESIVE BOND FAILURES IN AIRCRAFT HONEYCOMB-SANDWICH COMPOSITES

INTRODUCTION

Many military (as well as commercial) aircraft employ adhesives in place of metal fasteners for bonding and joining structural parts. One of the more successful applications of this technique has been in the fabrication of honeycomb-sandwich panels. In this design the aircraft skin is bonded to a honeycomb core to provide a lightweight, rigid, high-strength composite. Unfortunately, the bond requirements in high-performance aircraft are beginning to exceed the performance of the adhesives. Accordingly, aircraft operating in Southeast Asia have sustained numerous adhesive bond failures apparently attributable to the high humidity and temperature. Although these failures have not been catastrophic, maintenance and repair costs are extremely high, and the out-of-service time during repair increases the requirement for backup aircraft to insure completion of military missions.

Because of the important advantages of adhesive bonding over other means of fastening, solutions to these failures are sought in order that continued and increased use may be made of this type of construction. Some of the advantages of adhesive bonding are (a) greater strength-to-weight ratios, (b) greater fatigue resistance since the adhesive bond efficiently transfers the loads and stresses through the complete bond area as opposed to metal fasteners which concentrate stresses at the location of each metal fastener, (c) greater potential for making a more aerodynamically perfect surface, and (d) cheaper construction costs.

DEFINITION OF PROBLEM

At the outset, NRL scientists visited several naval repair facilities and aircraft and adhesive manufacturers to study the possible causes of these failures and to determine what might be done to improve the reliability of the bonded joint. The facilities visited were:

Naval Air Rework Facility, MCAS, Cherry Point, N.C.,
Naval Air Rework Facility, NAS, Norfolk, Va.,
Grumman Aircraft Corp., Bethpage, N.Y.,
General Dynamics Corp., Fort Worth, Tex., and
Bloomington Division of American Cyanamid Co., Havre de Grace, Md.

Based on first-hand observations and discussions with technical personnel at these facilities, the primary cause of bond failure appears to be the sensitivity of the bonded joint to moisture. This sensitivity takes two forms: first, the moisture migrates to the adhesive/substrate interface and displaces the adhesive bond with the water molecules, and second, and much more complex, the moisture or contaminated water provides an electrolyte for galvanic corrosion of the aluminum skin, with the resultant destruction of the bond. Bond failure also may be partially attributed to the brittleness of the adhesive.

During periods of stress, the adhesive may crack and weaken the bond. In addition, these cracks provide paths for water to enter into the bond from edges exposed to the atmosphere.

Attempts to pinpoint the exact failure mechanisms are further complicated in that one can never be certain that a high-quality bond was attained in the first place. Flaws, voids, or any inhomogeneity in a bond cause a stress concentration which can be a point of failure initiation. Although these flaws may not lead initially to a loss of strength in the adhesive, under service conditions they may rapidly grow to where they represent a critical deficiency in the bond.

BONDING AND ADHESIVE STUDIES

One of the most crucial stages in the preparation of an adhesive bond is during the actual bonding process itself. The morphology of the adhesive matrix formed during the bonding process is of prime importance to the strength and durability of the bond. However, only seldom is it possible to directly observe occurrences in the joint during or after bonding; the bond must be broken apart to be observed. Although useful information may be obtained from studying these broken or sheared bonds, other important features of the bond are destroyed and thus cannot be studied.

This section describes an effort to examine the undisturbed joint by observing the bond formed between two glass microscope slides. It should be emphasized that although the observations and photomicrographs were made on an adhesive bonded to a glass surface, these same features were observed when the adhesive was bonded to aluminum foil, which was subsequently removed by dissolution with NaOH.

The adhesive (FM61) employed in these experiments is one that has been used extensively in honeycomb-sandwich structures. It is a composite film supported by a nylon fabric carrier consisting of a modified epoxy adhesive on one side of the carrier and a nitrile elastomer on the other side. The composite adhesive was bonded between two cleaned glass slides according to the manufacturer's recommended cure conditions (350°F under 15-psi pressure for 60 min). The bond thickness was approximately 10 mils. In the photomicrographs which follow, the view is through the glass slide to the adhesive.

One of the first observations was the fairly large difference in the flow characteristics of the two adhesive resins, the modified epoxy and the nitrile elastomer. Under the recommended bonding conditions of pressure and temperature, much more epoxy resin is squeezed out of the bond line than nitrile elastomer. As a consequence, the resin thickness on opposite sides of the nylon cloth will be different. In fact, as the epoxy resin is squeezed out, the nylon cloth is pushed to, or close to, the interface of the resin and glass adherend. Close examination of the epoxy side of the composite adhesive (Figs. 1 and 2) reveals the presence of nylon filaments at or near the glass/epoxy interface. Another important feature, obvious in these two photomicrographs, is the presence of entrapped "air" bubbles. The odd shape of some of these results from the nylon filament running through or forming a boundary on the edges of the bubble. It also can be observed that a number of these air bubbles or voids are interconnected by the nylon filaments.

Figure 3 is a photomicrograph taken at lower magnification and shows the wide distribution of "air" bubbles in the adhesive. Figure 4 is a good picture of the features in the interface, although it is a somewhat misleading view in that the areas that appear high (closer to the observer) are actually below the areas that appear lower. Thus, the entrapped "air" bubbles appear to be rising out of the adhesive at its interface with the glass. This is not the case and the illusion results from the transmitted oblique lighting.



Fig. 1 - Photomicrograph from the epoxy side of the epoxy/glass interface showing the epoxy/nylon-cloth/nitrile-elastomer composite adhesive. Bonded between two microscope slides at 350°F and 15 psi pressure. (80X; transmitted light.)

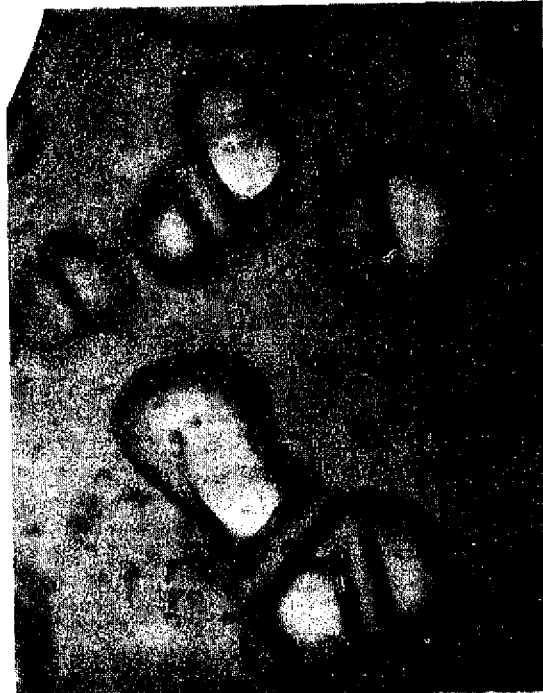


Fig. 2 - Photomicrograph from the epoxy side of the epoxy/glass interface showing the epoxy/nylon-cloth/nitrile-elastomer composite adhesive. Bonded between two microscope slides at 350°F and 15 psi pressure. (100X; transmitted light.)



Fig. 3 - Photomicrograph from the epoxy side of the epoxy/glass interface showing the epoxy/nylon-cloth/nitrile-elastomer composite adhesive. Bonded between two microscope slides at 350°F and 15 psi pressure. (40X; transmitted light.)



Fig. 4 - Photomicrograph from the epoxy side of the epoxy/glass interface showing the epoxy/nylon-cloth/nitrile-elastomer composite adhesive. Bonded between two microscope slides at 350°F and 15 psi pressure. (100X; transmitted, oblique light.)

Regardless of this distortion, features of the entrapped bubbles, nylon filament, and the intersection of the nylon filaments with the bubbles are plainly visible.

From these observations, it appears that the glass is completely wetted at the interface and covered by the epoxy resin and that no "air" bubbles are in direct contact with the glass. It was possible to observe through the microscope what appears to be a thin orange-colored film between the bubble and the glass. The presence of the adhesive layer at the interface between the bubble and the glass was revealed when the microscope was focused on the bubble, causing the thin adhesive layer to move out of focus and disappear. Then, as the microscope was refocused on the glass/resin interface, the skin again became visible.

Studies of the nitrile-elastomer side of the composite adhesive did not reveal as many structural features. It was not possible to conclude whether the nitrile adhesive completely wetted and covered the glass surface in every instance, although it appeared that it had in many cases. Figure 5 is a low-power photomicrograph of the nitrile-elastomer side as seen by transmitted light. The bubbles appear to be substantially below the interface and apparently are the same ones observed from the epoxy side. However, in another slide, bubbles or voids were seen which appeared to be at or near the glass/nitrile adhesive interface. These can be seen in Figs. 6 and 7. It is not possible to determine the depth of these voids, but it appears that some are quite deep and may extend through the bond to the epoxy/glass interface. The photomicrograph in Fig. 8 is

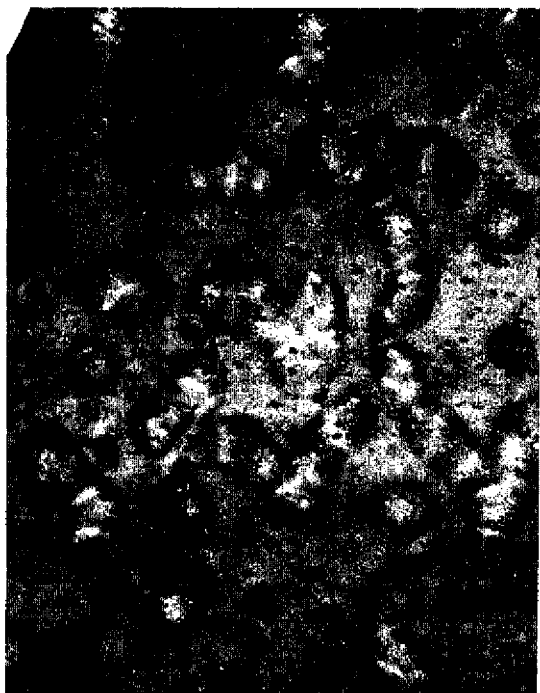


Fig. 5 - Photomicrograph from the elastomer side of the nitrile-elastomer/glass interface showing the epoxy-nylon-cloth/nitrile-elastomer composite adhesive. Bonded between two microscope glass slides at 350°F and 15 psi pressure. (40X; transmitted light.)



Fig. 6 - Photomicrograph from the elastomer side of the nitrile-elastomer/glass interface showing the epoxy-nylon-cloth/nitrile-elastomer composite adhesive. Bonded between two microscope slides at 350°F and 15 psi pressure. (80X; side lighting.)

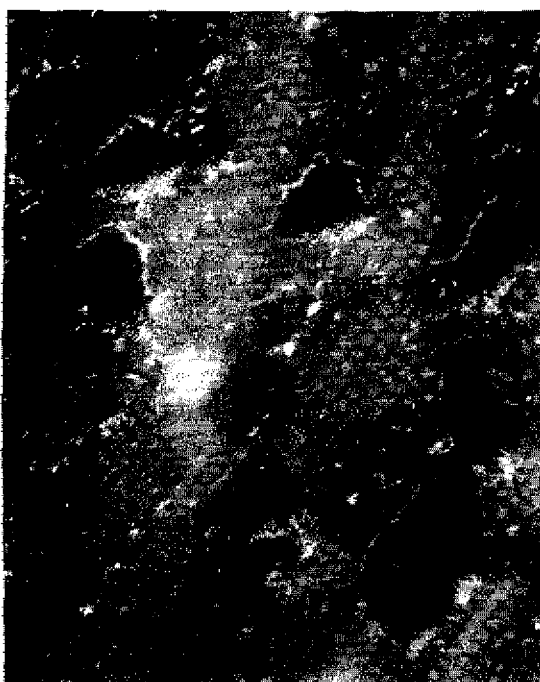


Fig. 7 - Photomicrograph from the elastomer side of the nitrile-elastomer/glass interface showing the epoxy/nylon-cloth/nitrile-elastomer composite adhesive. Bonded between two microscope glass slides at 350°F and 15 psi pressure. (80X; side light.)



Fig. 8 - Photomicrograph from the elastomer side of the nitrile-elastomer/glass interface showing the epoxy/nylon-cloth/nitrile-elastomer composite adhesive. Bonded between two microscope glass slides at 350°F and 15 psi pressure. (100X; transmitted, oblique light.)

similar to that in Fig. 4 in that a somewhat distorted view results from the type and angle of lighting (transmitted, oblique). In this particular instance, the microscope is focused below the interface and the view is through a thin layer of the nitrile adhesive. The shadow areas are the entrapped "air" bubbles in the adhesive matrix.

The nature of the large number of small irregularly shaped "particles" that appear in all the photomicrographs has not been determined. Some of these particle-like objects appear to be small entrapped air bubbles; it is possible that others are dirt or insoluble resin particles.

From these observations it is quite obvious that the bond contains a number of voids. These voids may be entrapped air and/or gaseous by-products formed during the cure of the adhesives. Thus, when the adhesive film is placed between the adherends to form a sandwich structure, air undoubtedly is entrapped between the adherends and the adhesives. During the cure, this air appears to be at least displaced from the interface as the adhesive wets and spreads on the adherend, but not necessarily displaced from the interfacial region of the bond. From observations on the uncured adhesive, it appears that a large source of these bubbles may result from air entrapped in the adhesive itself during manufacturing, and particularly in the epoxy component of the composite adhesive. In addition, the fact that the entrapped bubbles are more easily observed on the epoxy side of the cured bond is further evidence that the epoxy resin may be the major source of the entrapped bubbles. Examination of a modified epoxy adhesive film containing no

cloth support revealed a substantial amount of entrapped air throughout the entire matrix in both the uncured and the cured film. Since this film was simply cured in an open aluminum cup in an oven, the bubbles must have originated from within the adhesive itself.

In addition to the air entrapped in the film, volatile by-products (dissolved air, traces of solvent, decomposition products, and low-molecular-weight impurities) evolved during the cure of the adhesive might contribute substantially to the number of entrapped bubbles in the bond. Although specifications limit the volatile content of the composite adhesive to not more than 1.2% by weight, this weight of gaseous matter can be a substantial proportion of the total bond volume. As illustrated by the simplified calculation below, the ratio of the theoretical gaseous by-product volume to the bond volume is approximately 8.8 to 1.

Calculation of Volume of Adhesive Volatiles

A. Adhesive Properties —

adhesive weight = 0.075 lb/sq ft

adhesive thickness (uncured) = 0.015 in.

adhesive thickness (cured) = 0.010 in.

Assume volatile content is 1% by weight. (Maximum allowed by manufacturer's specifications is 1.2%.)

B. The volume of 1 sq ft of adhesive bond —

area \times thickness = V_{adh}

= 144 sq in. \times 0.010 in.

= 1.44 cu in. = V_{adh} .

C. The volume of the volatiles given off during the cure —

$V_{vol} = NRT/P$, where

$T = 177^\circ\text{C}$ (or 450°K)

$P = 2$ atm (1 atm above atmospheric pressure)

$R = 0.08205$ liter-atm-degree $^{-1}$ -mole $^{-1}$

N is estimated as follows:

wt. volatiles (lb) = $0.075 \times 0.01 = 0.00075$ lb (for 1% volatiles)

wt. volatiles (grams) = $0.00075 \times 454 = 0.340$ gram

Assume avg. mol. wt. of volatile products is 30 (presuming volatile products would be such species as CO , N_2 , $\text{CH}_2=\text{CH}_2$, CH_3OH , etc.).*

Thus $N = 0.340/30 = 0.0113$ mole.

So,

$$V_{vol} = \frac{0.0113 \times 0.08205 \times 450}{2} = 0.209 \text{ liter, or}$$

$$V_{vol} (\text{cu in.}) = 0.209 \times 61.0 = 12.7 \text{ cu in.}$$

*Even if the average molecular weight of the volatile by-products were 4 to 8 times the value assumed, the volume would still be substantial.

$$D. \text{ Ratio} = \frac{V_{\text{vol}}}{V_{\text{adh}}} = 12.7/1.44 = 8.8.$$

Thus, even if all air entrapment could be prevented in the manufacturing of the adhesive and in the bringing together of the bonding surfaces, the voids from the volatile by-products could be quite substantial. If the volatiles escaped from the edges of the joint with a degree of difficulty equal to that of the loss of the resin from the joint, then the bond would contain approximately 90% voids. However, since the void content in these bonds was obviously below 50% (but maybe as high as 10%), it is quite apparent that a smaller volume of volatile by-products is formed than theoretically calculated and/or most of the volatiles escape through the adhesive to the edges of the bond.

More data is needed before a model of the bonding process can be designed for this adhesive system. However, certain features can be proposed based on the information collected. Under the bonding conditions, more epoxy adhesive than nitrile elastomer is squeezed out of the joint. As a result, the nylon cloth is pushed toward the adherend interface with the epoxy to give perhaps a resin-poor region, while the nitrile-elastomer side of the cloth is resin rich. At the same time, the two resins appear to wet the adherend interface quite well and displace most of the air that is entrapped when the surfaces are initially brought together. However, numerous voids are produced in the bond matrix due to entrapped air or volatile by-products formed during curing. These entrapped bubbles appear to be concentrated more in the epoxy component than in the nitrile component, but some appear to span just about the complete thickness of the bond. These bubbles are also interconnected through the filaments of the nylon cloth, which may help provide paths for moisture migration into the bond.

Regardless of the possible source or sources for these entrapped bubbles, their presence is extremely undesirable. These voids not only lower the overall strength of the adhesive and provide points of stress concentration where crack initiations can occur, but they also increase the moisture susceptibility of the adhesive bond because of the porosity of the adhesive.

CORROSION STUDIES

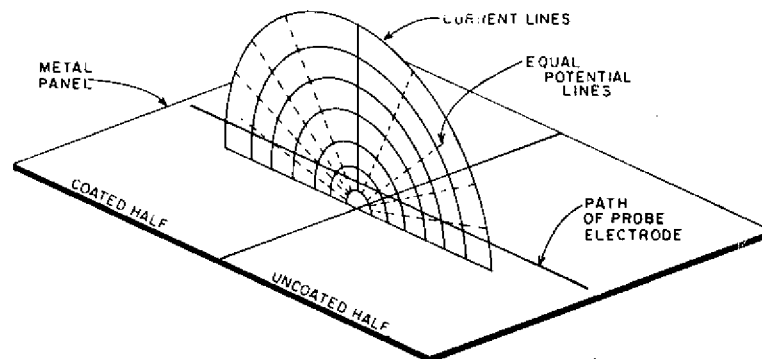
Most, if not all, of the aircraft honeycomb-sandwich delaminations and adhesive failures have been accompanied by corrosion of the bonded substrate. This corrosion is galvanic in nature and results from the contact of dissimilar metals used in the construction of the aircraft. Corrosion is most severe around metal fasteners which extend through the layers of skin laminates and hold the honeycomb panels in the air-frame structure. Since these steel fasteners are cadmium plated, the potential difference between the fastener and the aluminum skin would be expected to be small and provide only small corrosion currents. However, even small currents operating continuously eventually lead to extensive corrosion. This problem is further complicated by the fact that the cadmium plate often is scraped off the fastener, due to flexing of the structure during flight, thus exposing bare steel which has an even higher potential difference in contact with the aluminum. Further, high-strength aluminum alloys frequently are fastened to titanium and stainless steel components in structures, providing extensive potential for electrochemical interaction. As long as moisture can be excluded from such areas of contact, corrosion will not occur, but the paint currently used for this purpose cracks in a very short time. Breaks in the coating, along with voids in the adhesive and crevices in the structure, admit and trap moisture that may be contaminated with salt or other highly corrosive materials such as paint strippers. In such environments, corrosion will readily occur and destroy the adhesive bond.

Since most naval aircraft operate in highly humid environments and are exposed to sea water and rain, it appears almost impossible to avoid entirely corrosion under such conditions. However, it should be possible to retard greatly the process through anti-corrosive surface treatments or anticorrosive primers, and thus increase bond durability in this hostile environment.

Therefore, in view of the important role that corrosion appears to play in the destruction of the adhesive bond of honeycomb-sandwich structures, a practical means was sought for examining the effectiveness of proposed systems in preventing or retarding corrosion.

One method that appears attractive is an electrochemical technique, developed by Bharucha (1), for evaluating the effectiveness of pigmented paints in protecting metals from corrosion. With this technique, the effectiveness and the nature of this protection are determined by measuring the change in the solution potential over the anodic and cathodic regions of half-coated metal panels in a low-conductivity medium, for example, distilled water. The method is based on the fact that when a metal corrodes, a current flows and a potential distribution is induced in the solution between the cathodic and anodic areas, which is related to the corrosion on the surface of the metal (2). The change in this potential distribution induced by the interposition of different coatings is related to the effect of the coating on the corrosion process. Figure 9 shows a cross section of the current and potential distribution on a half-coated corroding metal panel. This cross-section is perpendicular to the panel and is exaggerated in comparison to the actual size of the panel for illustrative purposes. In general, the painted area is polarized such that it becomes cathodic to the unpainted area.

Fig. 9 - Electric current and potential distribution in the medium surrounding a corroding half-coated metal panel



The half-coated panel is placed in distilled water and scanned (as shown in Fig. 9) from the uncoated to the coated area a few millimeters above the surface with a probe calomel electrode. A reference calomel electrode is moved along parallel with, and at a constant distance from, the probe electrode. The position of the reference electrode is such that it does not traverse the panel; that is, the position is such that it is unaffected by the corrosion currents and potentials over the panel. As the half-coated panel is traversed by the probe electrode, the potential change is plotted as a function of the position of the probe electrode relative to the uncoated/coated boundary. Since the potentials measured are for the solution above the panel, changing the sign gives the corresponding potential on the surface of the panel.

The apparatus designed to make these measurements is shown in Fig. 10. The panel under study is placed in the glass tray containing the distilled water. The probe electrode

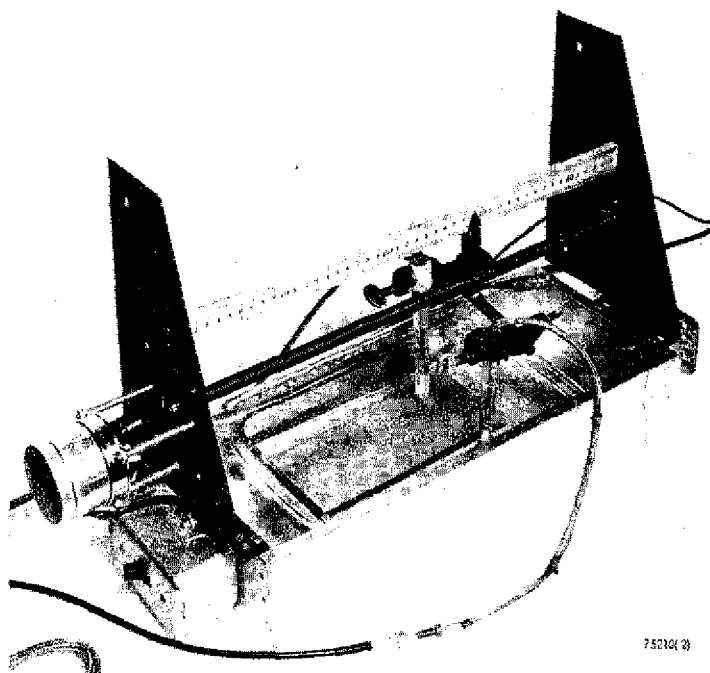


Fig. 10 - Apparatus for measuring the electrical potential distribution of half-coated metal panels in a corrosive medium

is positioned a few millimeters above the surface of the panel, while the reference electrode is positioned approximately 2 in. to the side of the panel. The electrodes are approximately 4 in. apart and are mechanically attached to the threaded rod so they move on parallel paths. The electrodes are driven at 1 cm/5 min by a clock motor attached to the threaded rod. The scan is started 5 cm before the boundary and stopped 5 cm past the boundary. The output of the electrodes is fed into a high-impedance Leeds & Northrup millivolt meter which is used to drive a strip chart recorder to give a continuous potential distribution as a function of the distance of the probe electrode from the boundary between coated and uncoated areas of the panel.

The shape of the curve reveals the effectiveness of the coating in preventing corrosion and whether this effectiveness results from chemical inhibition (at the cathode and/or anode) or a physical barrier inhibition, or both. Thus, by examining different coatings on the same metal substrates in the same medium, the effectiveness of the coatings can be compared.

Figure 11 illustrates two types of curves that can be obtained. Curve 1 is typical of protection that is due purely to the physical barrier of the coating. If the coating were thicker, the curve would have the same general shape, but would be compressed (i.e., electrical potential varies inversely with coating thickness). Curve 2 is characteristic of chemical inhibition, as well as physical inhibition, and is indicative of effective inhibition even a short distance into the uncoated area of the panel. The chemical inhibition is indicated by a change in the S-shape curve; a decrease in the potential value over the anodic region indicates anodic inhibition, while a decrease in the cathodic region, as illustrated in curve 2, indicates cathodic inhibition.

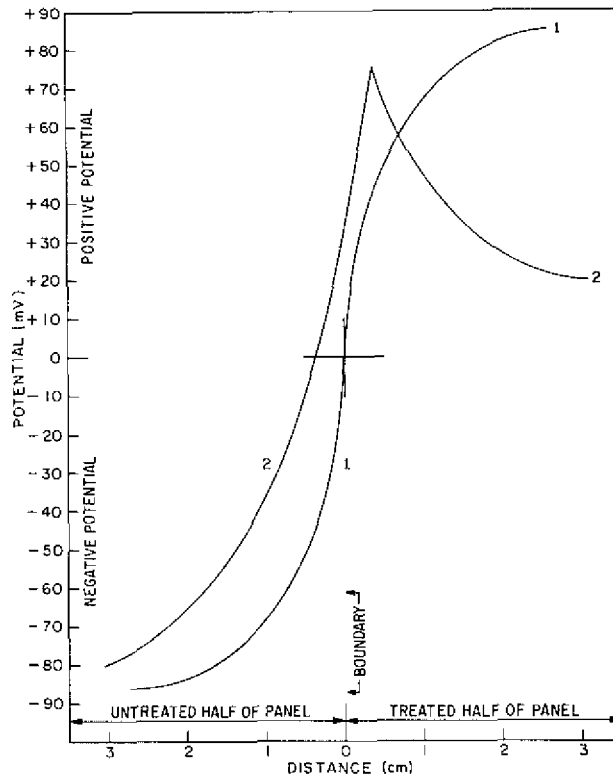


Fig. 11 - Typical electrical potential distribution curves for partially coated metal panels

Several other workers have made use of this technique. Rao, Yaseen, and Aggarwal (3) studied the corrosion of half-coated steel panels in distilled water and found their observations agreed with actual exposure tests. Legault (4) used this method to study relative tendencies of bimetallic couples and half-coated panels to corrode in salt solutions and concluded that the measurements indicated the effectiveness of a coating in protecting a metal substrate from corroding.

A number of specially treated and coated panels have been examined with this apparatus. Results with steel panels generally have been reproducible and consistent. However, aluminum, which is of prime interest, has not behaved so nicely. Table 1 lists the aluminum systems studied thus far. In order to obtain good measurements the panel must be actively corroding and in an equilibrium state. Since aluminum is much more resistant than steel to corrosion and builds up a protective oxide coating, corrosion currents are small and/or continuously changing.

To illustrate the technique and to show that cathodic and anodic areas could be detected, measurements were made on an aluminum/copper couple. This couple consisted of blocks of copper and aluminum held together at their edges by means of two rubber bands. The potential distribution of this couple in distilled-deionized water is shown in Fig. 12. As expected, the aluminum is anodic and has a negative potential. At the boundary, the potential reaches its maximum and then rapidly declines until it becomes positive over the cathodic copper. The two curves are repetitive runs in the same water and give an indication of the degree of reproducibility that might be expected. The only difference

Table 1
Treated Aluminum Panels Studied in Electrical Potential Distribution Measurements

Metal Substrate	Treatment or Coating*	Panel Designation
Alclad 7075-T6	Chromic acid anodizing	
Alclad 7075-T6	Alclad stripped off	T, W
Alclad 7075-T6	Alidine 1200	S
Alclad 7075-T6	Iridite #14-2	R
Alclad 7075-T6	Adhesive primer 227A [†]	Q, O
Alclad 7075-T6	Adhesive FM61 [†]	O
Alclad 7075-T6	Adhesive primer Br 127 [†]	X
Bare 7075-T6	Adhesive primer Br 127 [†]	AC
Bare 7075-T6	Adhesive primer, strontium chromate [‡]	AD
Bare 7075-T6	Adhesive primer, zinc chromate [‡]	AF
Bare 7075-T6	Adhesive primer, calcium chromate [‡]	AH
Bare 7075-T6	Adhesive primer, zinc tetroxy chromate [‡]	AK
Bare 7075-T6	Adhesive primer, mag. silicate [‡]	AM
Bare 7075-T6	Adhesive primer, Cellite 281 [‡]	AO
Bare 7075-T6	Adhesive primer, Al silicate [‡]	AQ
Bare 7075-T6	Adhesive primer, K tripolyphosphate [‡]	AS

*Only one-half of the panel is treated.

[†]Bloomington Division of American Cyanamid.

[‡]Epoxy/polyamid/pigmented adhesive primer prepared at NRL.

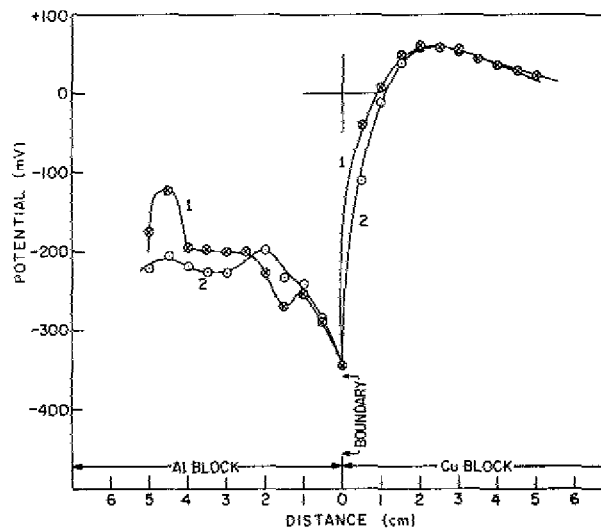


Fig. 12 - Electrical potential distribution of an aluminum-copper couple in distilled-deionized water

in the two runs was that the couple had to be repositioned after the first scan, and therefore on the second scan the probe electrode may not have followed the exact same path across the couple.

In Fig. 13 two potential distribution curves are shown for 7075-T6 alclad aluminum panel, half of which was anodized in a chromic acid bath. The nonanodized alclad area is anodic to the anodized area, and therefore the alclad corrodes. The two curves represent consecutive runs on the same panel in distilled-deionized water. The curves indicate both a physical barrier inhibition and some chemical inhibition. Since the curves are compressed compared to observations made on coated systems, the thin film produced in anodizing would appear to produce a highly effective physical barrier to corrosion. The deviation from the standard S-shape curve in the cathodic and the anodic regions indicates both cathodic and anodic inhibition of corrosion. Further, since the potential becomes cathodic before the probe electrode crosses the clad/anodized boundary, the anodize treatment provides protection in the untreated area near the boundary. The anodic chemical inhibition probably is attributable to chromate ions trapped in the coating during anodizing in chromic acid. This protection from corrosion in the boundary region of half-anodized panels has also been observed on panels exposed in the salt fog. The reason for the slight cathodic inhibition is not known.

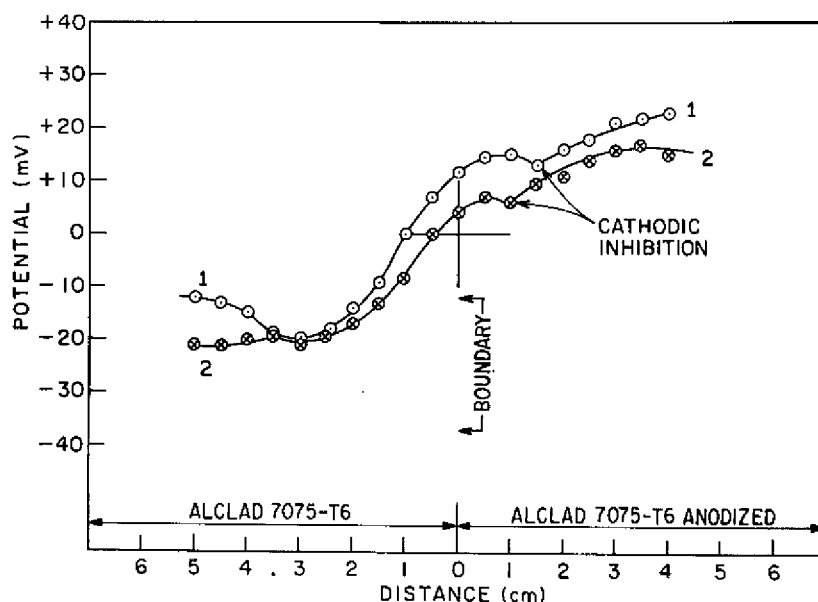


Fig. 13 - Electrical potential distribution of a half-anodized alclad 7075-T6 aluminum panel in distilled-deionized water

The importance of the potential-distribution curve during active corrosion is illustrated with the aluminum panel half coated with a strontium chromate anticorrosive adhesive primer. In Fig. 14, curve 1 shows the potential distribution of the coated panel 24 hr after preparation but before exposure to a corrosive medium, while curve 2 is the potential distribution of the panel after exposure to a salt fog overnight. Both measurements were made in distilled-deionized water. If the panel is soaked in distilled water and rinsed several times, the potential distribution again becomes very similar to curve 1. The shape of curve 2 indicates that the adhesive primer anodically inhibits corrosion.

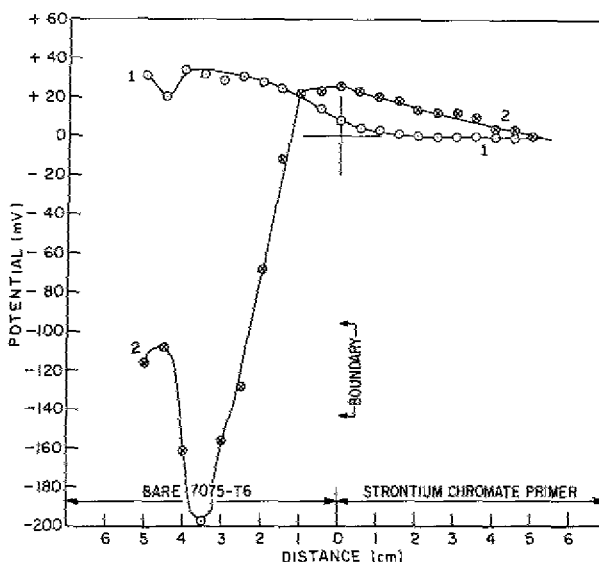


Fig. 14 - Electrical potential distribution of a bare 7075-T6 aluminum panel half coated with a strontium chromate adhesive primer in distilled-deionized water

In addition, the primer also provides corrosion protection for the uncoated metal at a substantial distance from the boundary. This protection has been confirmed experimentally by extended exposure of the test panel to the salt fog.

So far, most of these measurements have been made in distilled water. Of particular interest will be an extension of the method to solutions at different pH (this has already been done with a few of the panels by using organic buffers) and to water containing such additives as H_2S , SO_2 , salt, etc. Finally, it is felt that this technique will also be applicable to stress-corrosion studies.

CORROSION-INHIBITING PRIMERS AND TREATMENTS

In the previous section, mention was made of anticorrosive adhesive primers. Paints are used effectively for prevention of corrosion by employing primers containing anticorrosive pigments. The same approach also should be effective for adhesives, provided that the pigmented primer does not lower the strength of the joint. An anticorrosive primer should provide protection not only to the coated area but also to uncoated boundary areas, and areas where the primer has been damaged, exposing bare metal. This induced protection in the uncoated areas is desirable since, in the construction of the aircraft, holes for fasteners (often cadmium-coated steel) must be drilled through several layers of bonded skin, exposing reactive fresh metal surfaces. If the anticorrosive pigments cannot protect the exposed metal in the freshly drilled holes, then intergranular corrosion can start and progress along the corrosion-sensitive grain boundary areas, resulting in serious exfoliation of the metal and destruction of the bond.

An epoxy/polyamide system was selected in which to evaluate the pigment performance. The basic composition of the adhesive primer is shown as follows.

Epoxy resin	14.0% Epon 1001
Curing agent	4.2% Versamid 140
Pigment	7.2% pigment
Solvent	72.8% toluene/isopropyl alcohol (1:1)
Pigment dispersement agent	1.8% MPA-60

Nonvolatile content, wt/% — 27.2; pigment/binder ratio (wt) — 1.0/2.5

The pigments were dispersed in both the Epon 1001 solution and the Versamid 140 solution to determine their stability and their compatibility with each resin. None of the pigments showed any reactive instability in the resin solutions. The dispersions were made by grinding overnight in a pebble mill. In most cases the pigments settled out in an hour or so but were easily redispersed on mild shaking. A few of the pigments remained suspended for several days. It is felt that the suspension stability can be improved with any of the pigments, but at this stage the suspension problem was secondary and no improvement was sought.

Table 2
Summary of the Effect of Various Pigments in an Epoxy Matrix
on Inhibiting Corrosion of Bare 7075-T6 Aluminum

Pigment	Coating Thickness (mil)	Results
Zinc chromate	0.5	Corrosion protection at boundary and in score marks, as well as coated areas
Strontium chromate	0.8	Corrosion protection at boundary and in score marks, as well as coated areas
Calcium chromate	0.6	Corrosion protection at boundary and in score marks, as well as coated areas
Zinc tetroxychromate	0.6	No corrosion protection at boundary, but protection in score marks and coated area
Aluminum silicate	0.6	No protection in boundary or score area, but some protection in coated area
Magnesium silicate	0.4	No protection in boundary or score area, but some protection in coated area
Silica	0.7	No protection in boundary or score area, but some protection in coated area
Potassium tripolyphosphate	2.2	Some initial protection in boundary, but after a few days' exposure the coated area was corroded worse than the uncoated area

The primer was prepared by mixing the proper amounts of the pigmented epoxy and polyamide solutions. This mixture was allowed to stand for 30 min and then applied by brush to one-half of one side of bare 7075-T6 aluminum panels. The panels were air-dried for 15 min and then cured at 150°C for 10 min. The pigments and film thickness of the coatings are listed in Table 2. The panels were scored and then exposed to a 5% salt fog (pH = 6.8) at 95°F for a 90-day period. Zinc chromate appeared to be the most effective pigment, although zinc, strontium, and calcium chromate each provided protection in

the boundary region and in the scored area. Zinc tetroxychromate gave no protection at the boundary but did provide some protection in the scored area. All chromate pigments appeared to protect the metal beneath the coated area, while the unprotected aluminum corroded severely. The potassium triphosphosphate initially provided some protection in the scored and boundary regions, but at the end of 90 days it had permitted the worst corrosion of the series, and the coated area appeared to be much more severely attacked than the uncoated area. The aluminum silicate and the magnesium silicate provided little or no protection in the boundary or scored areas; however, the coated area was better protected than the uncoated metal, although there were a number of blisters in the coatings.

The condition of these panels at the end of 70 days is shown in Figs. 15 through 22. The photographs show discoloration in some parts of the score marks. The cause of this discoloration is probably due to the attack of $(OH)^-$ ions which are produced in the cathodic reaction

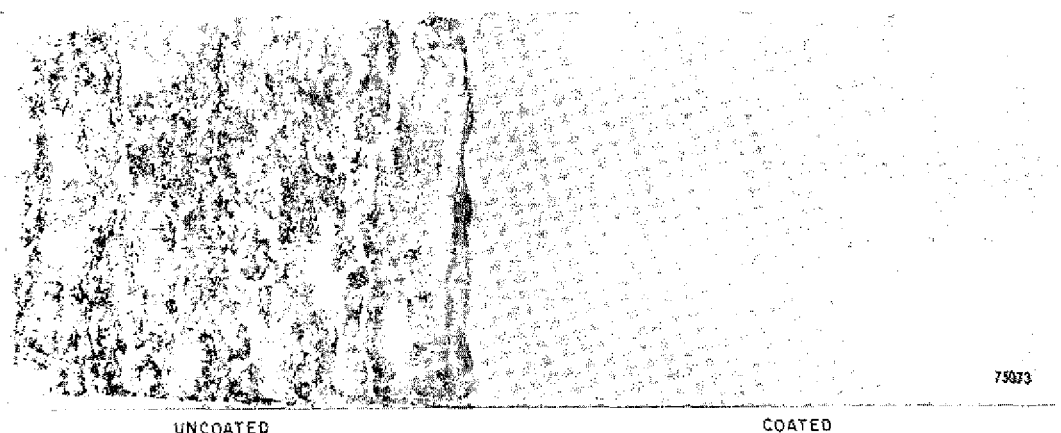


Fig. 15 - Epoxy/polyamid/zinc chromate primer on a bare 7075-T6 aluminum panel after 70 days' exposure to 5% salt fog

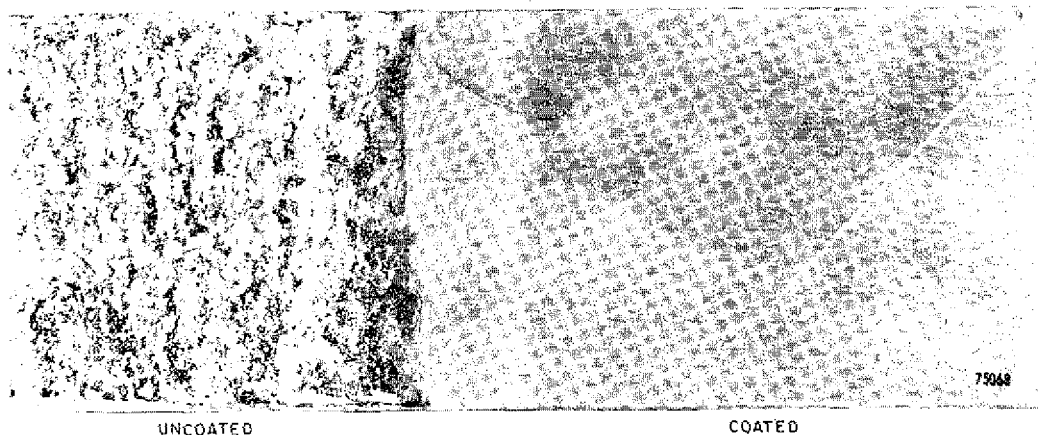


Fig. 16 - Epoxy/polyamid/strontium chromate primer on a bare 7075-T6 aluminum panel after 70 days' exposure to 5% salt fog



Fig. 17 - Epoxy/polyamid/calcium chromate primer on a bare 7075-T6 aluminum panel after 70 days' exposure to 5% salt fog



Fig. 18 - Epoxy/polyamid/zinc tetroxychromate primer on a bare 7075-T6 aluminum panel after 70 days' exposure to 5% salt fog

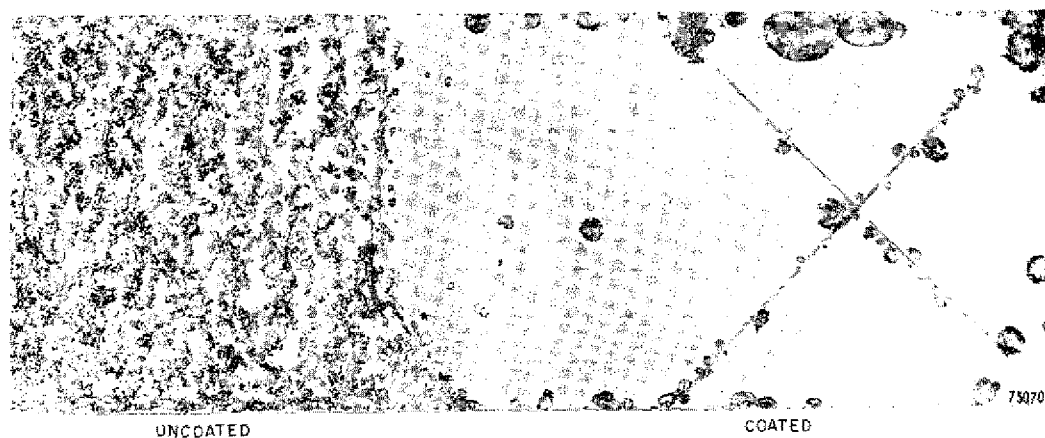


Fig. 19 - Epoxy/polyamid/aluminum silicate primer on a bare 7075-T6 aluminum panel after 70 days' exposure to 5% salt fog

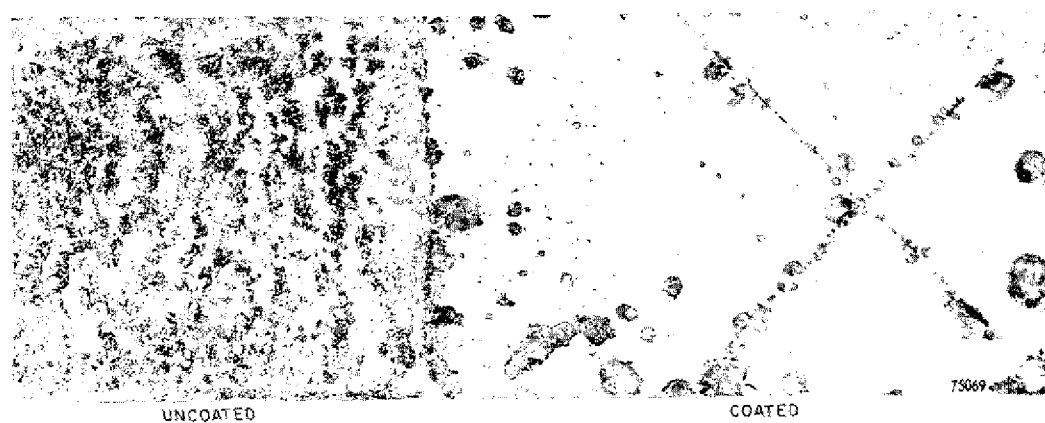


Fig. 20 - Epoxy/polyamid/magnesium silicate primer on a bare 7075-T6 aluminum panel after 70 days' exposure to 5% salt fog

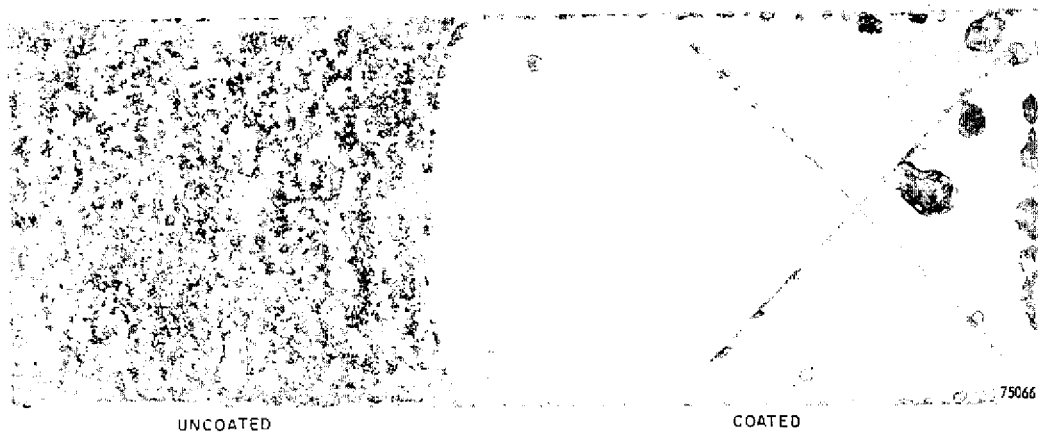


Fig. 21 - Epoxy/polyamid/silica primer on a bare 7075-T6 aluminum panel after 70 days' exposure to 5% salt fog

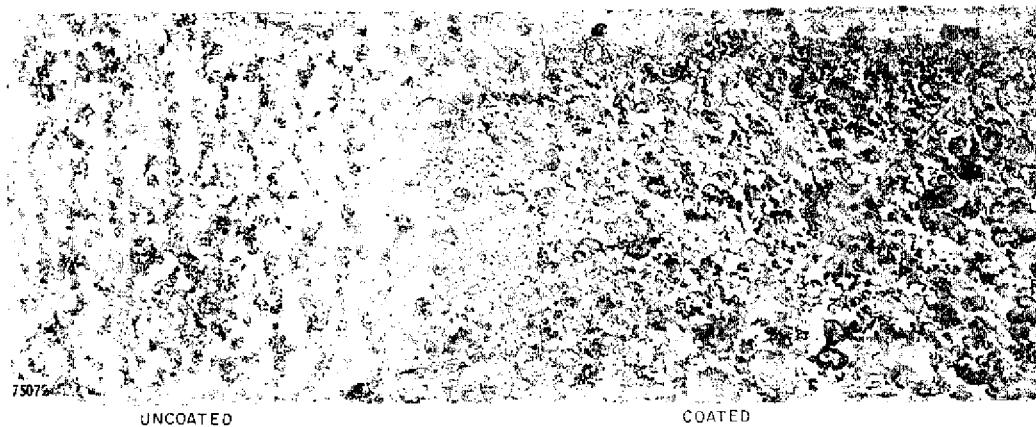
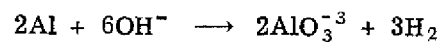


Fig. 22 - Epoxy/polyamid/potassium tripolyphosphite primer on a bare 7075-T6 aluminum panel after 70 days' exposure to 5% salt fog

The hydroxyl ions may then attack the exposed aluminum by the reaction



The results of these studies indicate that an anticorrosive primer can be an effective means for inhibiting corrosion in a bonded joint. Zinc, calcium, or strontium chromate would be effective, and the final choice would depend on their effect on adhesive strength and bond durability.

Other treatments on aluminum alloys were investigated. For these studies, the potentials of the panels in a 5% salt solution and distilled water were measured relative to a saturated calomel electrode before and after exposure in the salt fog. Measurements in distilled water were not always reproducible since the potentials varied with time and were slow to reach equilibrium. Examples of the behavior observed are shown in Table 3.

After approximately 5 min, the potential measurements in the 5% salt solution became fairly constant, but in distilled water the potentials were still changing after 30 min. (These unstable measurements in distilled water help to account for some of the problems in making the potential distribution measurements described in the previous section.) Since it was felt that corrosion in contaminated water was of more significance than measurements in distilled water, only the potentials in a 5% salt solution are reported for the various panels in Table 4.

Table 3
Electrical Potentials of 7075-T6 Alclad and 7075-T6 Bare Aluminum Panels
Immersed in Distilled and 5% Salt Water as a Function of Time

Medium	Immersion Time	Electrical Potential (Volts)	
		7075-T6 Alclad	7075-T6 Bare
Distilled Water	Initial	-0.311	-0.400
	5 min	-0.352	-0.365
	30 min	-0.329	-0.278
5% Salt Solution	Initial	-0.785	-0.688
	5 min	-0.813	-0.698
	30 min	-0.811	-0.698

It has been suggested that bonding should not be made to clad surfaces (5). The idea was that since the aluminum clad (which is essentially pure aluminum) has a slightly larger negative potential than aluminum alloys, it would be anodic with respect to the alloy. Therefore, the clad would be sacrificial and "used up" in preference to the base alloy, and thus any bond to it would be destroyed.

The results summarized in Table 4 show no relation between the extent of corrosion of the panels in the 5% salt fog and the magnitude of the potential in a 5% salt solution. The reason for this is that the potential under measurement is the difference between the panel as a whole and the saturated calomel electrode. The potential which affects corrosion, however, is the potential difference between the cathodic and anodic areas in the panel. Thus, even though the alclad panel has a larger negative potential (that is, more anodic) than the base alloy, it was the base alloy which was attacked first and most seriously corroded, and not the alclad. (Compare data for panels B, C, and E, with D and F.) In fact, when the alclad was mechanically stripped off half of a 7075-T6 alclad panel, it was the clad-free area that corroded most seriously even though the two were in direct contact. Thus, the potential difference between the cathodic and anodic areas within the alclad panel may be much smaller than the difference between these areas in a bare base-alloy panel. Similar behavior was observed with a 7075-T6 alclad panel, half of which was anodized in a chromic acid bath. Although the anodized half had a potential of -0.931 V and the nonanodized side a potential of only -0.908 V, the anodized half showed no sign of attack in the salt fog while the alclad half was slightly attacked.

It is apparent that reactivity alone does not determine the corrosion rate. Iron will corrode much more readily than aluminum, even though aluminum is the more reactive metal in the electromotive series. The fact that aluminum can form a protective oxide layer greatly retards its corrosion. Thus, it is also possible that the alclad forms a more protective oxide layer than can the base alloy itself.

Table 4
Summary of Salt Bath Exposure and Electrical Potential
Measurements in 5% Salt Solution Before and After Exposure

Panel	Type Aluminum	Potential in 5% Salt Solution (Volts)*		Appearance After 10 Days' Exposure
		Before Exposure to Salt Fog	After Exposure to Salt Fog	
B	7075-T6 alclad	-0.811	-0.907	Light corrosion
C	7075-T6 alclad	-0.802	-0.911	Light corrosion
E	7075-T6 alclad	-0.820	-0.904	Light corrosion
D	7075-T6 bare	-0.698	-0.764	Heavy corrosion
F	7075-T6 bare	-0.698	-0.761	Heavy corrosion
G	7075-T6 alclad with $\text{Na}_2\text{Cr}_2\text{O}_7$ - H_2SO_4 treatment	—	-0.902	Heavy corrosion
H	7075-T6 alclad, anodized in chromic acid	—	-0.894	No corrosion
I	7075-T6 alclad, half anodized:			
	anodized half	—	-0.931	No corrosion
	alclad half	—	-0.908	Slight corrosion

*Relative to saturated calomel electrode.

Although these observations are not fully understood, it appears that using alclad protection on high-strength aluminum alloys is a desirable practice and that bonding to an alclad surface does not seem to present a problem. Further studies will be made in this area.

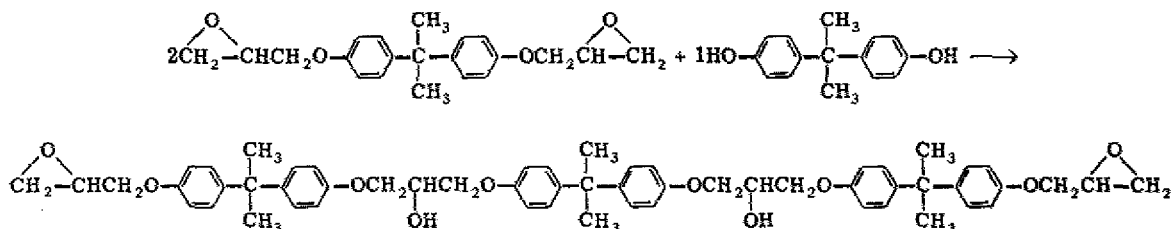
Also reported in Table 4 is the result from the salt fog exposure of a H_2SO_4 - $\text{Na}_2\text{Cr}_2\text{O}_7$ treated 7075-T6 alclad panel. It is of some interest and concern that this treatment greatly increased the susceptibility of the 7075-T6 alclad to corrosion. It is of concern because this is a standard treatment given most aluminum alloys before adhesive bonding. Further investigations will be made to verify this initial observation. If this observation is confirmed, and if it is characteristic of most aluminum alloys, then this treatment should be eliminated as a routine practice.

NEW ADHESIVE SYNTHESIS

The polymers which are more extensively used and which possess the more desirable properties for aircraft structural adhesives are the epoxy resins. However, in a number of cases in which high-performance aircraft must operate under severe environmental conditions, deficiencies in the epoxies appear to be at least partially responsible for failure of the bonds in honeycomb-sandwich structure. These adhesive deficiencies include

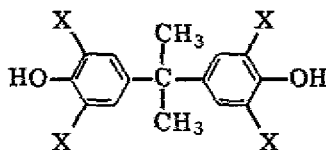
brittleness, excessive volatile evolution during cure, insufficient bond strength at elevated temperature (450°F), and inadequate moisture resistance. Since epoxy resins do possess high adhesive strength, any improvement in the properties listed would enhance their value in this application. In addition, materials are sought that can be prepared on a large scale, that is, resins which could be economically manufactured.

A survey of the literature revealed that a new epoxy resin intermediate (Epon 829) manufactured by the Shell Chemical Company might provide some degree of versatility and improvement. This intermediate is a precatalyzed liquid epoxy designed to react with varying amounts of bisphenol A to produce the higher-molecular-weight homologues of the basic epoxy resin, the diglycidyl ether of bisphenol A (for example, Epon 1001, 1002, etc.) (6). The reaction is illustrated by the following equation where the final molecular weight is dependent on the ratio of the bisphenol-to-epoxy-resin intermediate:



The Shell Co. points out that this reaction has several advantages over the other methods for preparing the higher-molecular-weight homologues of epichlorohydrin and bisphenol A. Of particular interest is the fact that the catalyst used here will not promote the known side reactions of epoxy/epoxy homopolymerization and the epoxy-aliphatic hydroxyl condensation which cause chain branching and result in a more rigid, brittle resin. The reaction produces an essentially linear polymer. It is our intention to extend this reaction to other reactive dihydroxy aromatic compounds hoping to eliminate some of the deficiencies described. The reaction is easily carried out by simply heating the selected ratio of Epon 829/bisphenol to 350°F for 30 min. After the reaction, the new resin needs no further treatment and can be used as is.

Studies have indicated that certain halogenated resins possess improved wet fatigue strength compared to their nonhalogenated analogs. Thus, it is proposed to synthesize partially halogenated epoxy resins with substituted bisphenol A of the general structure:



to give epoxy resins with the following structure:

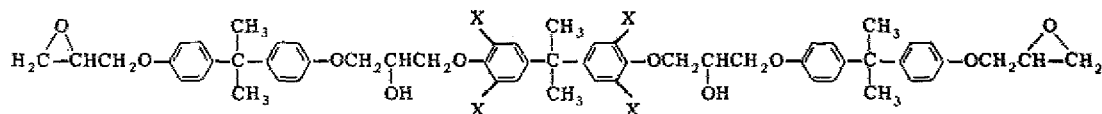


Table 5
Characteristics of Prepared Epoxy Resins

Parameter	Partially Chlorinated Epoxy Resin	Partially Brominated Epoxy Resin
Molecular weight	1146	1324
Weight per epoxy group	573	662
Weight-% halogen	12.4 Cl	24.2 Br
Approximate melting point	300° F	300° F

Epoxy resins, where the X shown above is Cl or Br, have been prepared with the characteristics reported in Table 5.

The moisture absorption characteristics of these two resins have been determined and compared to the nonhalogenated resin prepared in the same manner. For this study the epoxy resins were cured with an equivalent amount of metaphenylene diamine at 150°C for 3 hr. In addition, the cured resins were compared with a modified epoxy resin (FM96U) extensively used as an aircraft adhesive.

Exposure to moisture was in an oven at 40°C and 100% relative humidity. The results are reported in Table 6. The halogenated resins absorbed approximately one-third less water than the nonhalogenated resin, and all three absorbed a great deal less water than the normally specified aircraft adhesive resin.

Table 6
Water Absorption of Epoxy Adhesives

Adhesive	Exposure* (Days)	Wt-% Water Uptake
Aircraft Adhesive (FM96U)	14	2.82
Nonhalogenated Epoxy Resin	35	0.72
Partially Chlorinated Epoxy Resin	35	0.52
Partially Brominated Epoxy Resin	35	0.47

*40°C and 100% RH.

Differential thermal analysis of the resins cured with metaphenylene diamine revealed no difference in thermal stability between the halogenated epoxy resins and the nonhalogenated epoxy resins over the temperature range from room temperature to 235°C (455°F). The thermal curves were quite similar in all three cases.

The adhesive strength of these resins has not yet been determined; however, the studies thus far have indicated that the moisture absorption of an epoxy resin can be reduced by incorporating halogen into the structure without reducing the thermal stability over the temperature range of interest (450°F maximum).

SUMMARY

A number of approaches have been initiated to improve bond strength and durability of honeycomb core-sandwich structures, some of which are described in this report. The overall objective is to determine why and how these composites fail and then determine what can be done to eliminate or reduce these failures.

Failure, in part, appears to be caused by an undercutting type of corrosion which destroys the bond. The adhesives themselves appear also to be partially to blame. Although their initial strength is probably sufficient, their durability to environmental conditions is poor. The deficiencies in the adhesive are inadequate moisture resistance, high void content, and brittleness.

To correct these problems, corrosion-inhibitive primers and treatments are being studied, new water-resistant resins are being synthesized, and bonding procedures are being studied.

Although the current work deals with 7075-T6 alloy, both bare and alclad, other high-strength aluminum and titanium alloys will be studied.

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